ESRF	**Experiment title:** **Non-equilibrium kinetics in low molecular weight surfactant solutions**	**Experiment number**: SC-3001
Beamline: ID02	**Date of experiment**: from: 18 November 2010 to: 22 November 2010	**Date of report**: 28 February 2011
Shifts: 12	**Local contact(s)**: Dr. Jeremie Gummel, Dr. Theyencheri Narayanan	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

M. Sc. Grethe Vestergaard Jensen*, Aarhus University, Denmark
Prof. Jan Skov Pedersen*, Aarhus University, Denmark
Dr. Reidar Lund*, DIPC, San Sebastián, Spain
Prof. Juan Colmenero, DIPC, San Sebastián, Spain

Report:

The scope of the experiment was to study the equilibration of surfactant solutions from a non-equilibrium state achieved by rapid mixing in a stopped-flow apparatus on a millisecond time scale.

Surfactants self-assemble into at wide range of micelle structures depending on conditions such as concentration, temperature, ionic strength and pH. The process of self-assembly is very important in nature as well as in scientific and technological applications. The aim was to obtain a deeper understanding of the phenomenon and underlying factors. The self-assembly processes are fast, and it is the high flux synchrotron radiation that allows us to obtain the time-resolved structural information described below.

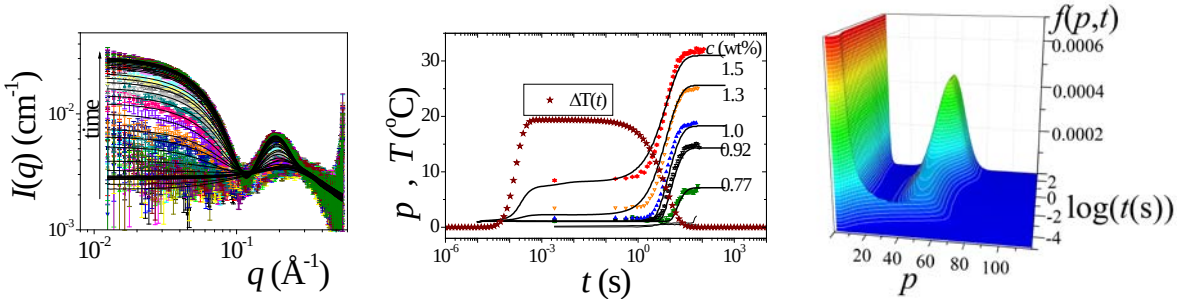

Figure 1. *a*: Data from mixing DDM in DMF with water 1:1. The final surfactant concentration is 1 wt%. *b*: Temperature increase, ΔT, upon mixing, and weight average aggregation numbers from Guinier fits to data at different surfactant concentraitons. Full lines are fits to a kinetic model. *c*: Evolution with time *t* of distribution of aggregation numbers *p* for the concentration of 1.5 wt% according to the fit of the kinetic model.

The aggregation of surfactant molecules into micelles was studied by rapidly mixing a solution of the surfactant dodecyl maltoside (DDM) in N,N-dimethylformamide (DMF) with water, leading to a drastic increase in the surface tension towards the hydrophobic surfactant tails, and thereby to micelle formation at concentrations above 0.7 wt%. The data (example in figure 1*a*) show how the micelle scattering contribution increases with time, indicating that the entire process from unimers to micelles is captured. The data were modelled on absolute scale by a linear combination of scattering from ellipsoidal micelles and singly dissolved surfactants (modelled as beads on a string). This structural model can be nicely fitted to the data. The experiment was repeated at five surfactant concentrations. The weight average aggregation numbers

extracted from the data were fitted with a mechanistic model, which only includes aggregation by step-wise insertion of single surfactants into the micelles (figure 1*b*).

The temperature increases upon mixing ($\Delta T > 0$ in figure 1*b*) since the water/DMF mixing is highly exothermic. It then decreases again during the experiment. The effects of the non-isothermic nature of the experiments were included in the mechanistic model. The model results give the evolution of the size distribution with time (example in figure 1*c*).

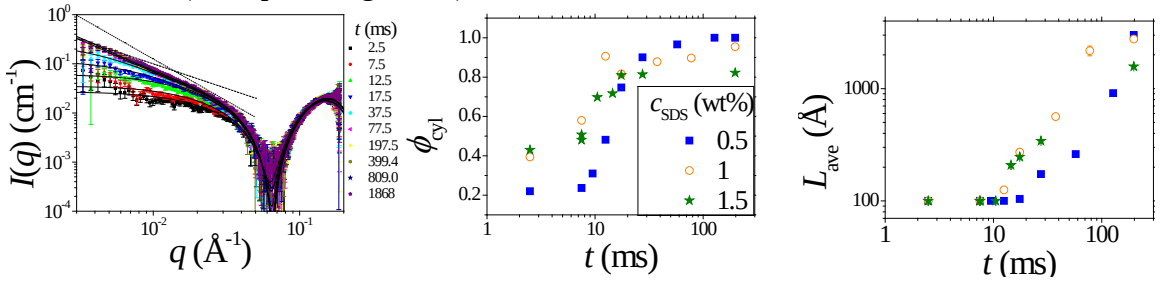

Figure 2. *a*: Stroboscopic SAXS data from mixing 2 M NaCl with a 2 wt% SDS solutions 1:1 (giving a final concentration of $c_{SDS} \approx 1$ wt%). Lines are model fits to data (see text). *b*: Fraction of surfactants in cylindrical/worm-like micelles from model fits. *c*: Length of cylindrical micelles.

Apart from micelle formation, two types of transitions from ellipsoidal to elongated cylindrical micelles were studied. One approach was to mix a solution of the surfactant sodium dodecyl sulphate (SDS) with a NaCl-solution, thereby screening the electrostatic interactions between the negatively charged head groups of SDS favouring a lower micelle surface curvature and an associated transition from ellipsoidal to cylindrical micelles. This process is clearly reflected by the data (example in figure 2*a*) by the increasing negative slope of the intensity at low values of the length of the scattering vector *q*. The data were modelled by a linear combination of scattering from ellipsoidal and cylindrical micelles. The cylinders are semi-flexible and worm-like for lengths exceeding the Kuhn length of approx. 600 Å. The fraction of surfactants in cylindrical micelles and the length of the cylinders/worms are shown in figure 2*b* and 2*c* (when mixing with 2 M $NaCl_{(aq)}$). The concentration dependence of the kinetics indicate that the ellispoids fuse to form the cylinders.

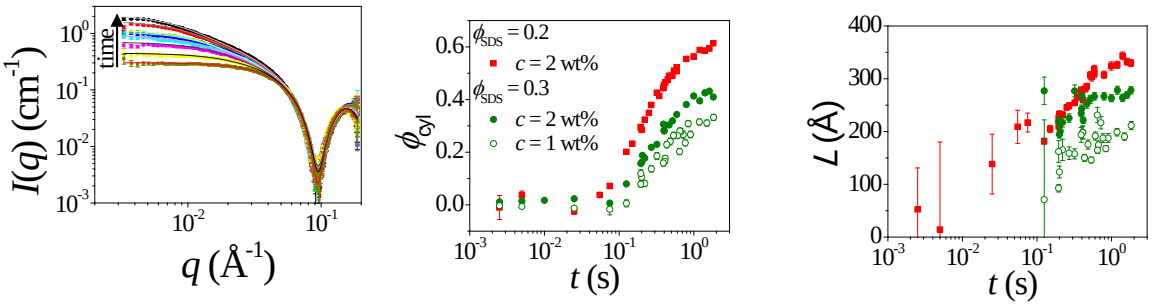

Figure 3. *a*: Stroboscopic SAXS data from mixing of a 3.2 wt% DDM and a 0.8 wt% SDS solution, both in 0.3 M NaCl 1:1, giving a total concentration of $c = 2$ wt%, and a weight fraction of SDS of $\phi_{SDS} = 0.2$. Selected data frames are shown. Lines are model fits to data (see text). *b*: Fraction of surfactants in cylindrical micelles from model fits. *c*: Length of cylindrical micelles.

Another approach to obtain a micelle elongation was to mix solutions of DDM and SDS. We have observed, that at certain SDS-DDM ratios ellipsoidal DDM and SDS micelles mix to form cylindrical micelles. We suggest that this is owing to the larger distance between the charged SDS head groups when the DDM and SDS molecules are mixed in the micelles. This again leads to weaker repulsions between the SDS head groups favouring a lower micelle surface curvature and transition to cylindrical micelles. The data (example in figure 3*a*) have been modelled by a linear combination of scattering from ellipsoidal and cylindrical micelles. The results for fraction of surfactants in cylindrical and for the cylinder lengths are shown in figure 3*b* and 3*c*, respectively. Before the cylinder formation at $t \approx 0.1$ s (from 0.01 to 0.1 s), the data indicate that the ellipsoids rearrange, reflected in changes in the contrast conditions and radial profile of the corona. This might be due to mixing of the surfactants, or another type of redistribution that then triggers the cylinder formation. The experiment was repeated at different DDM:SDS ratios and at different total concentrations. For both the SDS/NaCl and DDM/SDS mixing experiments, the high time resolution was acchieved by performing stroboscopic experiments, and the data prooved to be highly reproducible.

The results are great examples of how synchrotron radiation can give a unique opportunity to obtain a deeper understanding of the mechanisms of micelle formation and growth, and we expect to extract very interesting knowledge from them.